

Solid Superacid Catalysis: *n*-Butane Conversion Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia

Julie L. d'Itri, Tsz-Keung Cheung, and Bruce C. Gates
Department of Chemical Engineering and Materials Science
University of California
Davis, CA 95616

INTRODUCTION

Environmental concerns are leading to the replacement of aromatic hydrocarbons in gasoline by high-octane-number branched paraffins and oxygenated compounds such as methyl *t*-butyl ether. The ether is produced from methanol and isobutylene, and the latter can be formed from *n*-butane by isomerization followed by dehydrogenation. Paraffin isomerization reactions are catalyzed by very strong acids such as aluminum chloride supported on alumina. The aluminum chloride-containing catalysts are corrosive, and their disposal is expensive. Alternatively, hydroisomerization is catalyzed by zeolite-supported metals at high temperatures, but high temperatures do not favor branched products at equilibrium. Thus there is a need for improved catalysts and processes for the isomerization of *n*-butane and other straight-chain paraffins. Consequently, researchers have sought for solid acids that are noncorrosive and active enough to catalyze isomerization of paraffins at low temperatures. For example, sulfated zirconia catalyzes isomerization of *n*-butane at temperatures as low as 25°C (1). The addition of iron and manganese promoters has been reported to increase the activity of sulfated zirconia for *n*-butane isomerization by three orders of magnitude (2). Although the high activity of this catalyst is now established (2, 3), the reaction network is not known, and the mechanism has not been investigated.

The goal of the research was to investigate low-temperature reactions of *n*-butane catalyzed by iron- and manganese-promoted sulfated zirconia. *n*-Butane was chosen as the reactant because it is a potentially valuable source of *i*-butane.

EXPERIMENTAL

Iron- and manganese-promoted sulfated zirconia was prepared by incipient wetness impregnation from sulfated zirconium hydroxide (Magnesium Elektron, Inc.) that was impregnated with iron and with manganese nitrates. The weight percentages of iron, manganese, and sulfur in the catalyst were 1.0, 0.5, and 1.8 %, respectively.

Before each catalytic reaction experiment, the catalyst in flowing N₂ (30 mL(NTP)/min) was heated from 20 to 450°C at a rate of 7.1°C/min, and the temperature was then held at 450°C for 1.5 h. Reactions were carried out in a once-through plug-flow reactor at atmospheric pressure and temperatures in the range 40-225 °C.

RESULTS

In the absence of a catalyst, no conversion of *n*-butane was observed. In the presence of the promoted sulfated zirconia catalyst, propane, *i*-butane, *n*-pentane, and *i*-pentane (with traces of methane, ethane, and hexanes) were observed as products. The selectivity for formation of *i*-butane from *n*-butane was greater than 85% for conversions less than 60%. At times on stream < 1 h, the carbon balance closed within $\pm 10\%$, and at longer times on stream this balance closed within $\pm 5\%$.

The *n*-butane conversion as a function of time on stream is shown in Figure 1 for the temperature range 40 to 100°C. There are two distinct regimes, a break-in period followed by a deactivation period. At the lowest reaction temperature, the conversion of *n*-butane was still increasing even after 4 h on stream. In contrast, at 75°C and at 100°C, the maximum conversion was observed after less than 1 h.

A linear correlation was observed between the maximum *n*-butane conversion observed in each experiment carried out at temperatures in the range 40-100 °C and the inverse space velocity. Thus the data demonstrate that these conversions are differential and determine reaction rates. However, catalyst deactivation was so fast at the higher temperatures that the maxima in conversion vs. inverse space velocity plots could not be discerned. Thus, the data at these higher temperatures do not determine the maximum conversions. Rates at these higher temperatures were calculated from conversions < 30% on the basis of the assumption that the conversions were still differential.

Rates of formation of the various products at 100°C are summarized Figure 2. Maxima in the rates of formation of each of the following products were observed as a function of time on stream at temperatures < 150°C, provided that the partial pressure of *n*-butane in the feed was < 0.005 atm: propane, *i*-butane, *n*-pentane, and *i*-pentane. Because of the break-in period, it was not possible to extrapolate these rates accurately to zero time on stream. Thus the values of the rates at the maxima are taken as the best available measures of the initial reaction rates (i.e., those characterizing the undeactivated catalyst).

The predominant product was *i*-butane, and thus it is concluded that the principal reaction was isomerization of *n*-butane. The observation of propane and pentanes suggests that disproportionation also occurred. The molar ratio of C₃ to C₅ approached a value of approximately 1.10 ± 0.05 at the lowest temperature investigated (40°C), after about 25 h onstream. Thus these data suggest that stoichiometric disproportionation and isomerization were virtually the only catalytic reactions taking place under these conditions. However, this simple result was not generally observed. Typically, the molar C₃/C₅ ratio was greater than unity. For example, after 3 h on stream at temperatures of 75 to 150°C, the ratio was in the range of approximately 1.5-1.7.

The ratio of C₃ to *i*-C₄ in the product is taken as an approximate measure of the selectivity for disproportionation relative to isomerization of *n*-butane. This ratio varied with reaction temperature and time on stream.

As the *n*-butane feed partial pressure increased, the rate of reaction increased, indicating the positive order of the reaction. Catalyst deactivation was least at the lowest *n*-butane partial pressure.

DISCUSSION

The data show that conversion of *n*-butane catalyzed by iron- and manganese-promoted sulfated zirconia at 40 °C gives propane, *i*-butane, and pentanes as the principal products, along with traces of methane, ethane, and hexanes. By far the predominant product was the isomerization product, *i*-butane. The same principal product has been observed for *n*-butane conversion catalyzed by unpromoted sulfated zirconia at 25°C; it was formed along with propane and traces of *i*-pentane (1). The activity of the promoted sulfated zirconia catalyst is higher than those of the other solid acid catalysts.

Hsu *et al.* (2) reported the first characterization of the promoted sulfated zirconia catalyst, investigating *n*-butane isomerization under approximately the same conditions as ours, but with a higher feed *n*-butane partial pressure (e.g., 0.58 atm). These authors estimated rates of the isomerization reaction by extrapolating conversions to zero time on stream to approximate the performance of the fresh catalyst. Zarkalis (4) investigated a catalyst similar to that of Hsu *et al.* and estimated activities of the fresh catalyst from the maximum rates measured as a function of time on stream (as in this work). In the work of Hsu *et al.* and that of Zarkalis, liquid *n*-butane was used as a feed which was vaporized before introduction into the flow reactor. In the work reported here, the butane was fed as a gas, and the *n*-butane partial pressures were typically 1-2 orders of magnitude lower than those used by Hsu *et al.* and Zarkalis. Thus, the rates reported by these workers are not directly comparable to the rates reported here. A rough comparison based on extrapolation of Zarkalis' data shows an order of magnitude agreement with our data.

The simplest product distribution observed in this work is consistent with a reaction network including only isomerization and stoichiometric disproportionation. At the lowest reaction temperature, 40°C, the C₃/C₅ molar ratio after the break-in period was nearly the stoichiometric ratio of unity for disproportionation, namely, 1.1, with an estimated experimental error of about ± 5%. The only other demonstration of a nearly stoichiometric paraffin disproportionation reaction was reported for *n*-butane conversion catalyzed by aluminum chloride supported on sulfonic acid resin at 100°C; the principal reaction was isomerization, which was much faster than disproportionation (5).

The observation of disproportionation products (5) suggests that a C₈ intermediate might have formed. This same suggestion was made by Bearez *et al.* (6, 7), who proposed a bimolecular pathway for *i*-butane conversions catalyzed by H-mordenite at about 350°C. According to their proposal, both the isomerization and disproportionation products could be formed from the C₈ intermediate. Reactions involving C₈ intermediates might be energetically favored over monomolecular isomerization because they would be expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of *n*-butane requires the formation of a primary carbenium ion, which is highly unstable (8).

The product distributions at the higher temperatures show that the reaction network must in general be more complex than just isomerization and disproportionation. The observed C₃/C₅ molar ratios were always greater than 1, suggesting the further reaction of C₅ products, which undergo cracking more readily than smaller paraffins (9). The results are not sufficient to demonstrate the stoichiometry of the cracking; they are consistent with the possible formation of C₉ intermediates. Cracking of a C₉ intermediate would give C₃ and C₆ products, among others, and trace amounts of C₆ products were observed. A C₉ intermediate would be formed only from secondary products of *n*-butane conversion, and therefore it is expected that the concentrations of these species were much lower than those of primary products.

The results suggest that the highly active solid superacid could be a practically useful catalyst for isomerization, which would be accompanied by disproportionation. It could be advantageous to operate at low temperatures to minimize the secondary reactions and to favor the branched isomerization products.

CONCLUSIONS

1. Iron- and manganese-promoted sulfated zirconia is a superacid that catalyzes *n*-butane isomerization and disproportionation at temperatures in the range of 40°C to 225°C.
2. The predominant reaction was isomerization with the rate of isomerization being 4.2×10^{-8} mol/(s · g of catalyst) with a feed *n*-butane partial pressure of 0.0025 atm at 75°C.
3. Under the same conditions the rate of formation of propane was 1.2×10^{-9} mol/(s · g of catalyst).
4. As the temperature increased, the selectivity for isomerization decreased and that for disproportionation increased.
5. Following an initial break-in period of about an hour, the catalyst underwent rapid deactivation.
6. The C₅ disproportionation products were partially converted to lower-molecular-weight products; the C₃/C₅ ratio increased with increasing temperature.
7. The solid superacid catalyst is potentially valuable for practical low-temperature paraffin isomerization accompanied by disproportionation of *n*-butane.

ACKNOWLEDGMENTS

We thank David Clough of Magnesium Elektron, Inc., for providing the sulfated zirconium hydroxide. The research was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center.

LITERATURE CITED

- (1) Hino, M., and Arata, K., *J. Chem. Soc., Chem. Commun.*, 851 (1980).
- (2) Hsu, C.-Y., Heimbuch, C. R., Arnes, C. T., and Gates, B. C., *J. Chem. Soc., Chem. Commun.*, 1645 (1992).
- (3) Jatia, A., Chang, C., MacLeod, J. D., Okubo, T., and Davis, M. E., *Catal. Lett.*, **25**, 21 (1994).
- (4) Zarkalis, A., M.Ch.E. Thesis, University of Delaware (1993).
- (5) Fuentes, G. A. and Guisnet, M., *J. Catal.*, **76**, 440 (1983).
- (6) Guisnet, M., Avendano, F., Bearez, C., and Chevalier, F., *J. Chem. Soc., Chem.*

Commun., 336 (1985).

- (7) Bearez, C., Avendano, F., Chevalier, F., and Guisnet, F., *Bull. Soc. Chim. Fr.*, 346 (1985).
- (8) Brouwer, D. M., in "Chemistry and Chemical Engineering of Catalytic Processes" (R. Prins and G. C. A. Schuit, Eds.), p. 137. Sijthoff and Nordhoff, Alphen an den Rijn, the Netherlands, 1980.
- (9) Pines, H., "The Chemistry of Catalytic Hydrocarbon Conversions," p. 83. Academic Press, New York, 1981.

LIST OF FIGURES

Figure 1. Effect of reaction temperature on *n*-butane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm at 75°C and 100°C and 0.005 atm at 40°C. Total feed flow rate = 80 mL(NTP)/min. Catalyst mass = 1.5 g.

Figure 2. Rate of product formation from *n*-butane catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm. Temperature = 100°C. Total feed flow rate = 80 mL/min. Catalyst mass = 1.5 g.

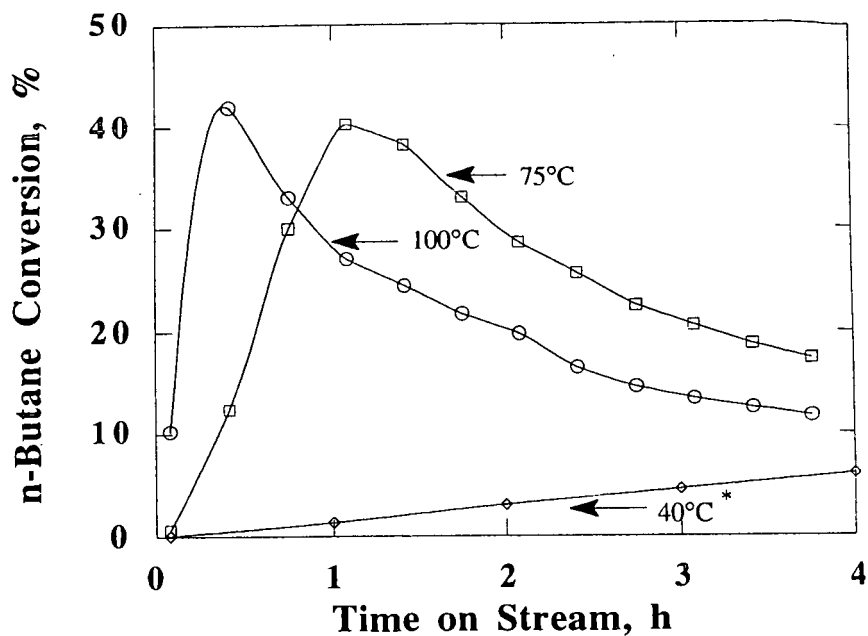


Figure 1. Effect of reaction temperature on n-butane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed n-butane partial pressure = 0.0025 atm at 75°C and 100°C and 0.005 atm at 40°C. Total feed flow rate = 80 mL(NTP)/min. Catalyst mass = 1.5 g.

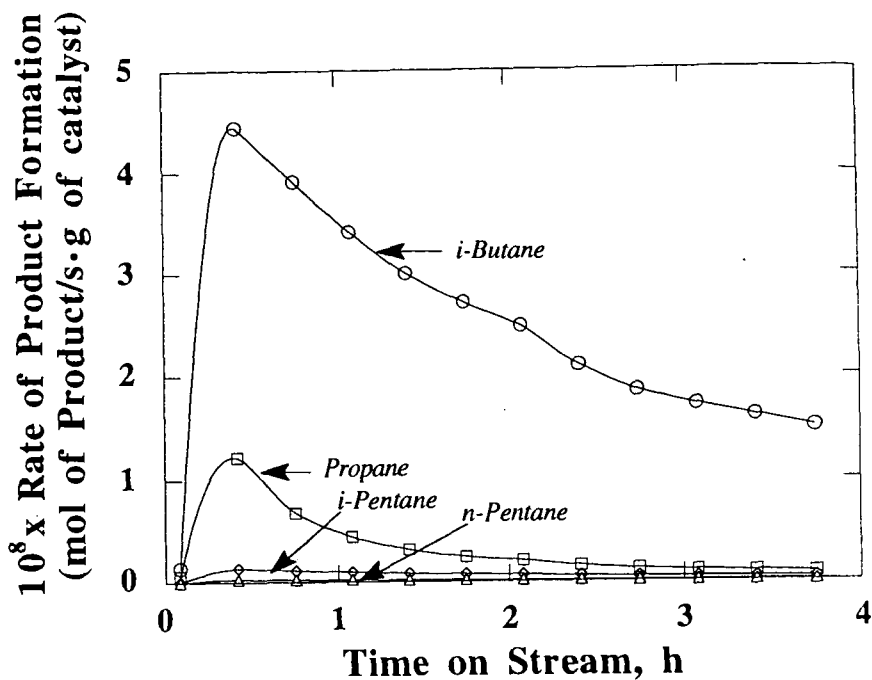


Figure 2. Rate of product formation from *n*-butane catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm. Temperature = 100°C. Total feed flow rate = 80 mL/min. Catalyst mass = 1.5 g.